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DRAWINGS ATTACHED

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(54) SAMPLE INTRODUCTION SYSTEM FOR MASS SPECTROMETER ANALYSIS

(71) We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The present invention relates to an improved arrangement for effecting the rapid introduction of a gaseous sample into a mass spectrometer analysis unit. More particularly, the invention is directed to a special tubular sample inlet system which, in part, utilizes an orifice type molecular leak as an inlet section and a stream spliting gas distribution means that cooperates in providing a continuous fast transfer of a sample stream to the analysis unit.

The usual types of sample withdrawal means for a mass spectrometer, whether periodic or continuous, utilize a capillary tube inlet so that merely a small portion of the material to be analyzed from a process or product stream will be withdrawn for transfer to the particular analysis unit. However, the capillary tube arrangement results in a slow, large surface area transfer passageway such that a portion of the stream, or condensate therefrom may be adsorbed on the wall of the tubing. Alternatively, a highly reactive components can undergo desired reactions with other accompanying constituents during the time period required to effect the transfer through the capillary tubing. For instance, in attempting to carry out the continuous sampling of an auto engine exhaust stream for the monitoring of entrained nitric oxide (NO) in a mass spectrometer unit, it is necessary to obtained a fast sampling operation to minimize adsorption of entrained hydrocarbons to the tube wall, as well as necessary to minimize the reaction of the nitric oxide with oxygen and other constituents in the stream. Preferably the sampling is attained in a period of time less than about 3 seconds. Also, it may be pointed out that an automotive exhaust stream is continually changing with varying operating speeds and conditions and rather continuous sampling is needed to obtain a proper analysis of any one component in such an exhaust stream.

This usual mass spectrometer, including those for nitric oxide monitoring, provides a slight vacuum for the sample intake. Thus, for the present type of sample introduction system the pressure differential involved is not too great, merely being from about 1 atmosphere in the auto exhaust line to a vacuum of about 10^{-6} milimeters of mercury as provided by the analysis unit. As a result, a preferred system uses a vacuum pump connection to bring the sample stream to the zone of the analyzer.

In addition to the use of capillary tube type inlet means for usual sampling systems, there have frequently been used glass frit discs, and the like, directly ahead of the analysis unit so as to limit the sample stream flow to such unit. However, systems using frits have no adjustability and tend to have operating difficulties because of dirt accummulations, particularly with auto exhaust gas streams which can provide carbon particles and condensation of hydrocarbons. Also, it has been found that certain frits, such as of sintered silicon carbide may tend to initiate or enter into a chemical reaction with certain of the exhaust constituents and thus provide still further difficulties in obtaining accurate analysis for nitric oxide or for any other particular component.

The present invention seeks to provide a gas sample introduction system for an analysis unit which provides for rapid withdrawal and shunting of a sample portion of a gaseous stream to the analyzer.

According to the present invention there is provided a sample introduction system for a mass spectrometer which is particularly adapted to effect rapid sampling of a gaseous

stream and preclude reaction of an entrained highly reactive material with other accompanying constituents, which comprises in combination, a molecular leak section positioned across and sealed to a sample withdrawal tube as an inlet means thereto, said leak section comprising a thin diaphragm having a small central opening of less than 0.004" diameter, and an adjustable outlet means from said sample tube providing two outlet passageways therefrom, whereby a vacuum source connected to one of the outlet passageways can pull a sample stream to the zone of said outlet means, said outlet means being then able to shunt an adjustable fractional portion therefrom through the other outlet passageway to said mass spectrometer.

A preferred design utilizes a thin foil membrane, as of gold, for the thin diaphragm member having the orifice opening to provide in effect "molecular leak". Actually, the tubings and molecular leak section provide an entire introduction system which are preferably of stainless steel or glass or other smooth substantially inactive type of material such that there will be a minimum of adsorption or retention of particulates or of any entrained gaseous components passing through the system. Also, as will be set forth more fully hereinafter, the outlet passageway means preferably utilizes an adjustable three-port valve where there is a means for adjusting the outlet flow from at least one of the outlet ports. Generally, in a conventional "splitter" valve or three-port valve there will be a straight through passageway for continuous flow of at least a portion of the fluid stream and an adjustable tapered plug in a needle valve type design from the second of the outlet ports of the valve unit.

Reference to the accompanying drawing and the following description thereof will serve to more clearly illustrate one embodiment of the improved sample introduction system for a mass spectrometer unit, as well as point out additional advantageous features which are obtained through the use of such specially constructed system.

Figure 1 of the drawing is a diagrammatic elevational type view indicating the arrangement for the rapid transfer of a sample stream through the improved introduction system to an analysis unit.

Figure 2 of the drawing indicates in a sectional view one means for attaching a thin gold foil membrane to the end of a tubular member so as to provide a molecular leak inlet section thereto.

Referring now particularly to Figure 1 of the drawing, there is shown a sample withdrawal tube 1 connecting to and projecting slightly interiorly of a line 2 which is carrying a stream that is to be analyzed for at least one entrained gaseous component. The inlet end of the sample withdrawal tube 1 is provided with a thin diaphragm member 3 having a small orifice opening 4 and clamp means 5. The latter is merely indicated diagrammatically and may constitute any suitable holding or clamping means that is capable of attaching the diaphragm member 3 to the end of the tube member 1. The diaphragm 3 is preferably very thin and in the nature of gold foil or other equivalent noble metal foil, whereby the depth of the passageway provided by orifice 4 is almost negligible.

For continuous sampling of a particular gaseous component, as for example nitric oxide in an automotive exhaust gas stream, the size of the orifice will often be about 0.002" in diameter and as a rule in the range of 0.0008" to 0.004" whereby only a very small fractional portion of the continuously flowing exhaust gas stream will be taken into the sample introduction system.

The tubing 1 is preferably kept relatively short in length, generally not more than about 2 feet long, and may comprise 1/4" tubing or other small diameter tubing in the range of about 1/8" to 1/2". As pointed out hereinbefore, preferably the tubing is supplied of stainless steel, glass or other smooth and chemically inert type of material. At least the material shall be non-reactive with the particular component to be analyzed in the mass spectrometer or other analyzer unit.

In the present drawing, the tubing 1 is shown connecting with one form of adjustable three-port valve unit 6, which again is preferably of stainless steel, glass, or the like. The valve 6 is provided with a straight through passageway 7 suitable for carrying gas or fluid from an inlet port section 8 to an outlet port 9 and thence into tubing 10, as well as suitable for effecting the shunting of a fractional portion of the stream through a small port 11 communicating with an outlet connection 12, in turn carrying to an analysis unit 13. The adjustable feature of valve 6 provides a turnable valve stem section 14 connecting between an exterior grip section 15 and an internal needle-like valve plug or projection 16. The latter moves within the outlet orifice opening 11 and meters the flow therethrough into the analysis unit 13.

In the present operation for effecting the rapid withdrawal of a sample gas stream and its introduction into a mass spectrometer type of unit, there will be a vacuum pump connection to line 10 and valve at port 9 such that there is a positive withdrawal and flow of a sample of gas through the inlet end of the system at the leak section 4. The withdrawn gas sample stream is thus continuously carried down into the straight through passageway 7 of valve 6 whereby a major portion of a stream will carry on to the vacuum pump means and a fractional portion shunted through the metered passageway

11 and outlet port 12 to be then introduced into analysis units 13.

When desired, there may be adjustment of the flow through port 11 by means of the moving stem 14 and needle valve means 16.

In Figure 2 of the drawing there is shown the utilization of standard tube fitting means for attaching a diaphragm or thin foil molecular leak member, such as 17, to the end of a sample withdrawal tube, being indicated as 18. The arrangement is, of course, of advantage in providing a simple means for having a removable screw cap member 19 effect the holding of an insertable diaphragm or leak member 17. In this case, the latter is clamped between the underside of cap member 19 and above compressor rings 20 and 21, with the later in turn being designed to fit against the inwardly sloping end of a standard tube connector fitting 22. The latter, in turn, is shown connecting to the tube 18 by means of an internally threaded member 23 which bears against internal compression ring members 24 and 25 encompassing the end of tubing 18 within the end of tube fitting 22.

It is, of course, not intended to limit the present invention to any one means for holding a diaphragm member and small molecular sized orifice leak across the end of a tube in order to provide the inlet to the latter, inasmuch as various clamping means will be obvious to those skilled in the art of working with tubular equipment.

In addition, modified means for providing the by-passing of a portion of the sample stream into the analyzer unit 13 may be provided other than through the use of an adjustable three-port valve, such as 6; however, the latter is of particular advantage in giving an adjustable control through a small open orifice and precludes the difficulties that are frequently obtained through the use of frits or other porous types of membranes which may be readily clogged by dirt or condensate. The adjustable nature of the valve means is also a valuable feature as noted hereinbefore in obtaining a desired controlled flow into an analysis unit which is to be continuously monitoring a flow stream.

WHAT WE CLAIM IS: —

1. A sample introduction system for a mass spectrometer which is particularly adapted to effect rapid sampling of a gaseous stream and preclude reaction of an entrained highly reactive material with other accompanying constituents, which comprises in combination, a molecular leak section positioned across and sealed to a sample withdrawal tube as an inlet means thereto, said leak section comprising a thin diaphragm having a small central opening of less than 0.004" diameter, and an adjustable outlet means from said sample tube providing two outlet passageways therefrom, whereby a vacuum source connected to one of the outlet passageways can pull a sample stream to the zone of said outlet means, said outlet means being then able to shunt an adjustable fractional portion therefrom through the other outlet passageway to said mass spectrometer.

2. A system according to Claim 1 further characterized in that said thin diaphragm comprises a gold foil.

3. A system according to Claim 1 or 2 further characterized in that said adjustable outlet means from the withdrawal tube comprises an adjustable metering three-port valve unit whereby a metered flow may be provided from at least one of the outlet ports at the valve unit.

4. A system according to any of claims 1 to 3 further characterised in that the inlet means, sample withdrawal tube and outlet means from the tube are of a material which provides a substantially smooth interior passageway and is substantially inert or non-reactive.

5. A system according to claim 1 and substantially as hereinbefore described or illustrated with reference to the accompanying drawings.

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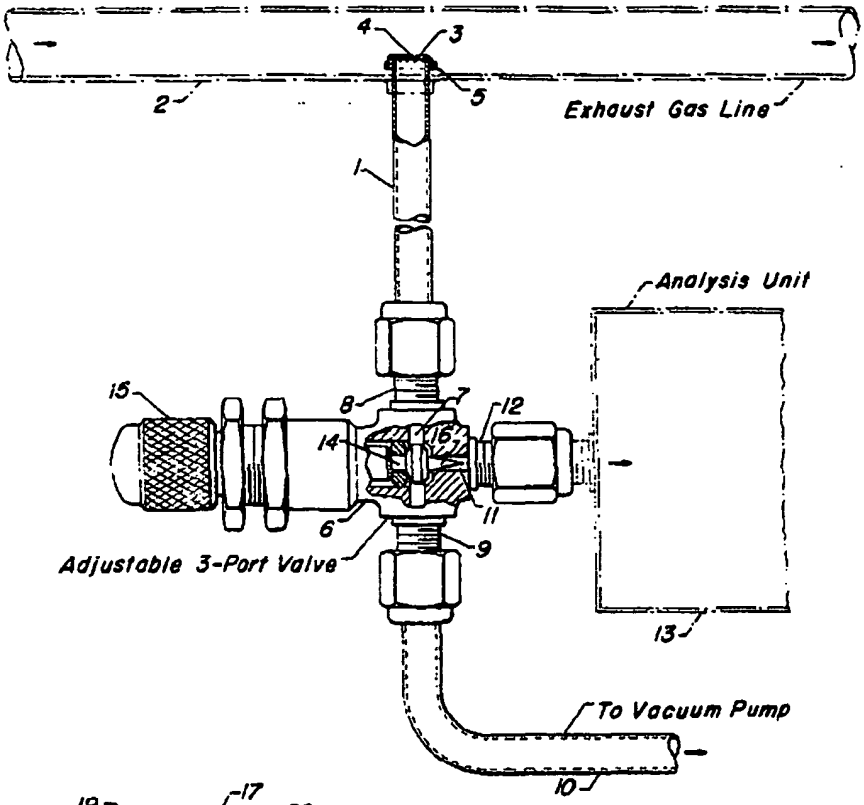
1224915 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

Figure 1



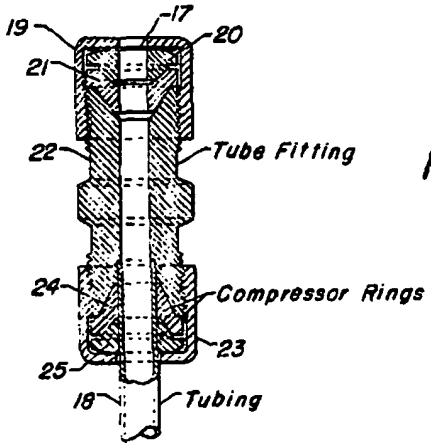


Figure 2